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Influence of a precursor solution on the characteristics of platinum on alumina catalysts

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S3 MICRO (HECUS) small angle diffractometer (Cu Kα, 50W) with a point collimation of primary beam was used for measuring scattering patterns of all samples. The scattering vector magnitude $q = 4\pi*\sin(\theta)/\lambda$ (where 2θ is the scattering angle, and $\lambda = 1.541$ Å is the radiation wavelength) was used as the scattering coordinate. The scattering intensity was measured within the range of the scattering vector magnitudes $0.01 < q < 0.6$ Å^{-1}. All measurements were performed in quartz capillaries. For precursor solutions the SAXS patterns of pure solvents were subtracted from the corresponding SAXS patterns of the platinum precursor solution taking into account the X-ray absorption coefficients. ATSAS software was used for the data treatment.[1] The radius of gyration of the particles (R_G) was determined by the slope of the small angle curve in coordinates ($\mathrm{Ln}(I(q); q^2)$.[2]

The mean size of the active component particles of the prepared catalysts was determined with high resolution transmission electron microscopy on a JEM-2010 (Jeol Co., Japan) with lattice resolution of 0.14 nm with accelerating voltage of 200 kV. The studied samples were bound onto the standard copper grids placed into the holder and put into the cell of the electron microscope. To determine the particle size Analysis ITEM v.5 software was used (Soft Imaging System Gmbh, 2004). For analysis the sets of 200-300 measured particles for each sample were used.

Catalytic tests were carried out in a flow-circulation reactor at atmospheric pressure.[3] Kinetic data were obtained for constant flow rate and inlet mixture composition (C_3H_8 – 1%; O_2 – 15%; He as

balance gas) at 300 °C. This device complies with the principles of recycle reactor and provides the gradientless mode, which allows measuring the activity of catalysts at a high accuracy due to the absence of temperature and concentration gradients inside the catalyst bed. The multiplicity of the reaction mixture circulation through the catalyst bed was about 50; which was sufficient to free the catalyst bed of the concentration gradient. The catalyst loading was adjusted to provide almost constant initial propane conversion (45±5%). It was found that such changes in the catalyst loading did not result in change of the measured activity. Gas chromatography equipped with flame ionization detector and methanator for precise determination of CO and CO_2 concentrations was used to analyze the outlet mixture composition.

Reaction rate W was calculated via equation:

$$W(ml/mol_{Pt} \cdot sec) = \frac{C_0(C_3H_8) - C(C_3H_8)}{m(g_{Pt})} \times u\left(ml/_{sec}\right) \times 195.1\ (g/_{mol}),$$

where m is the mass of Pt in the sample (g); $C_0(C_3H_8)$ and $C(C_3H_8)$ are initial and measured propane concentrations (vol. %), respectively; u is the flow of gas mixture.

Dispersion D_m was calculated with application of the mean diameter of Pt particles ($\overline{d_{Pt}}$) obtained from TEM measurements:

$$D_m = 6 \times V_m/a_m \times \bar{d}_{Pt},$$

where V_m is the atomic volume (nm^3), a_m is average area occupied by one Pt atom (nm^2); $V_m = M \times 10^{21}/\rho \times N_A = 0.0151\ nm^3$; $a_m = 1 \times 10^{14}/\sigma = 0.08\ nm^2$; M is molecular mass (195.1 g/mol for Pt); ρ is density (21.45 g/cm^3 for Pt); N_A is Avogadro constant ($6.02 \times 10^{23}\ mol^{-1}$); σ is the concentration of metal atoms at the surface ($1.25 \times 10^{15}\ cm^{-2}$ for Pt).

Turnover frequency values (TOF) were calculated via equation:

$$TOF(s^{-1}) = \frac{\overline{W}(ml/mol_{Pt} \cdot s)}{22400\ ml/mol \times D_m} \times 100\%,$$

where $\overline{W}$ is the average reaction rate; D_m is Pt particles dispersion, %.[3,4]

Elemental analysis was conducted with X-ray fluorescence method on ARL PERFORM'X analyzer with Rh-anode of X-ray source.

The tests on chemisorption capacity of the catalysts were performed using a pulse CO-chemisorption method.[5] Samples reduction was performed in H_2 flow (30 cm^3/min) at different temperatures. Temperature ramp was 4°/min. The apparent average diameter of Pt particles (d_s, nm) was calculated from CO-chemisorption data via equation:

$$d_s = 1.08/(CO/Pt),$$

where CO/Pt is the degree of dispersion equal to the ratio of the number of adsorbed CO molecules to the total number of supported Pt atoms.[6]

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